(12) UK Patent Application (19) GB (11) 2 293 388 (13) A

(43) Date of A Publication 27.03.1996

(21) Application No 9519044.3

(22) Date of Filing 18.09.1995

(30) Priority Data
(31) 4433419 (32) 20.09.1994 (33) DE

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(51) INT CL[6]
B01J 20/00 // G21F 9/12

(52) UK CL (Edition O)
C3V VCX
C1P PP P109
C3W W122 W213 W225 W305 W327
G6R R1C2
U1S S1122 S1356 S1434 S1435 S3020 S3021 S3022

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WPI Abstract Accession No80-22860c/13
&JP55022312A

(58) Field of Search
UK CL (Edition N) C3V VCX VDS VDX
INT CL[6] B01J
Online: WPI

(54) Liquid absorbent comprising internal spaces providing swelling capacity for binding liquid harmful materials

(57) A strewable liquid absorbent comprises an expanded mineral in combination with a swelling agent in which said mineral provides the swelling agent with space for swelling and conducts the liquid to the swelling agent. The mineral may be mica (vermiculite); the swelling agent, polyacrylate, rubber, alginate, silica gel, or bentonite. The absorbent may comprise a base or acid.

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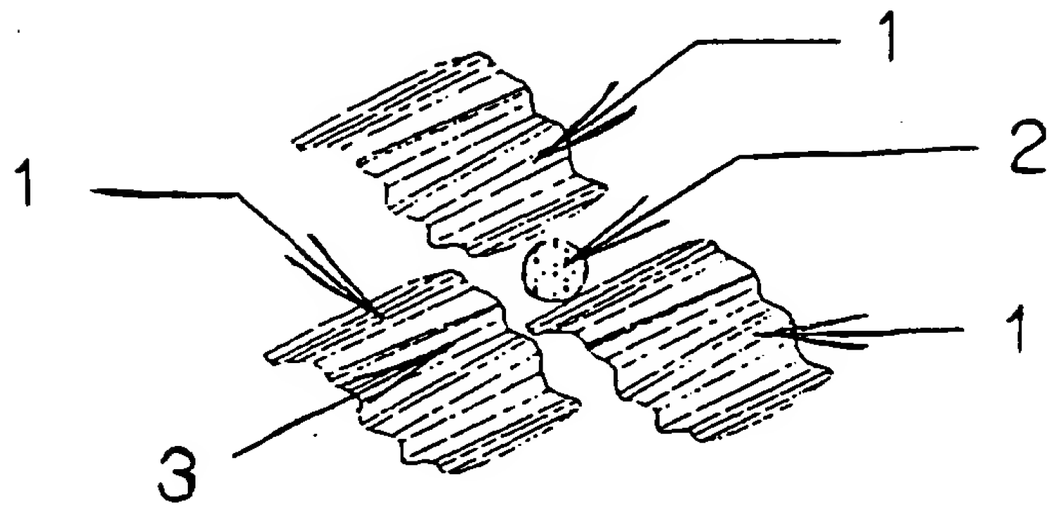

Fig.1

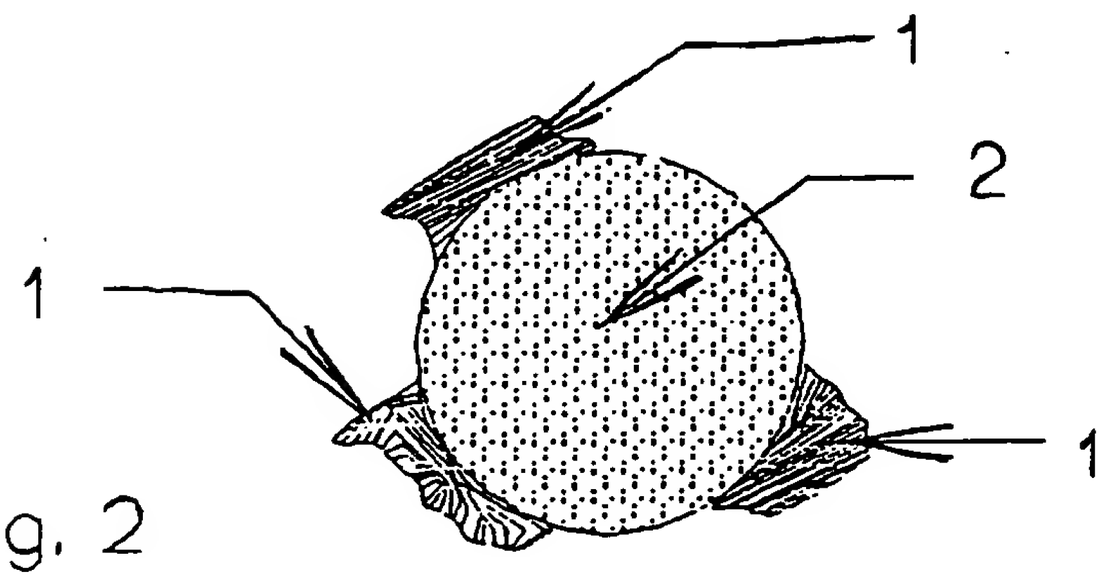

Fig. 2

Absorbent Comprising Internal Spaces Providing Swelling Capacity for Binding Liquid Harmful Materials

Strewable absorbents made of minerals or of organic materials have been known for absorbing liquids. However, these absorbents, depending on their rigidity, will in turn release a substantial part of the absorbed liquid under the action of pressure. There is also the danger of that the absorbents, when disposed of in a refuse dump, will relase considerable amounts of the absorbed liquid upon a wash-out with rain water.

There have further been known mineral and organic strewable swelling agents which, due to the swelling process, are capable of including liquids such as to resist a higher external pressure, while in the swollen state they can only be used to a limited extent because of their tackiness and, for example, undesirably will stick to the bottom and walls of disposal container.

A strewable absorbent has been known which consists of kieselguhr and a preferably water-binding polyacrylate as used, for example, in baby's napkins, where an absorption of leaked hazardous liquids is to be effected upon the addition of water. This is a particularly troublesome method to bind a liquid which has drained off. In addition, the amount of the pollutant is undesirably enlarged by the addition of water. If such a process is erroneously used with a liquid pyrophoric material that would undergo an explosive reaction with water, there would even occur a serious accident.

The present invention offers a safe process for the manufacture of an almost tack-free absorbent and a strewable application form for practical use, which absorbent is versatile and fast-acting to absorb run-off liquid polutants.

Moreover, the absorbent according to the invention is particularly suitable for consolidating or thickening liquid or liquid-containing hazardous waste and for wrapping and safely moving liquid or liquid-containing hazardous material and waste.

The absorbent according to the invention is also suitable for the safe tranportation of biologically hazardous solutions, for example liquids containing dangerous pathogens, microorganisms or bacteria, fungi or viruses.

The absorbent according to the invention, more particularly, satisfies the need for absorbing the pressures occurring in closed containers upon swelling in order to prevent a deformation of the transportation container or package and to bind the absorbed liquid so that the absorbent remains as much tack-free and strewable as possible and to facilitate controlled dispensing by the user.

In order to illustrate the process and the use of the absorbent according to the invention, an exemplifying formulation and solution to the problem is described.

For creating an absorbent for acids and lyes according to the invention, 100 parts by volume of an inflated expandable mica, also called 'vermiculite'. It is distributed by the company Rench Chemie GmbH under the tradename PERLEEN 444. The expandable mica has been won in South Africa and has a lamellar structure. Water of crystallization was included between the lamellae. The evaporating water of crystallization caused the mineral bodies to expand and produced numerous voids. It is the particular advantage inherent to such vermiculite that it may be squeezed

like a concertina and the lamellae are close enough to convey a liquid by capillary transportation.

The mineral bodies have a diameter of from 0 to 2 mm, the maximum being 6 mm. In this formulation, the vermiculite will serve the oject of the supporting bodies according to the invention.

Said vermiculite is admixed with 10 parts by volume of a dried polyacrylate of a cationic character and having a granular structure of from from 0 to 1 mm, the maximum being 2 mm. These polyacrylates are commercially available as swelling agents. One preferred product as used here is 'Acidsafe' by the company Stockhausen, affiliated to the Hüls group; said product, more specifically, is capable of swelling in acidic and alkaline solutions and of including such liquids. The polyacrylate is to serve as a swelling agent in this formulation.

Both of the components are mixed in the dry state. An additional use of adhesive agents is not required. The mixture is substantially stable to shipping, since the mineral bodies, due to their external structures, are capable of fixing the swelling bodies in the mixture. The result is a well-to-feel, nearly dust-free grain composition which is clean to be handled.

Now, this mixture is capable of absorbing acidic and alkaline solutions while remaining almost tack-free and strewable. The lamellar supporting bodies will immediately absorb the liquid and convey same to the swelling bodies.

The swelling bodies begin to absorb the liquid, thereby undergoing a considerable increase in volume. If the liquid would have been present in a closed container, then the swelling bodies now would exert a significant pressure onto the container walls. Now it is the particular property of the supporting bodies which advantage is taken of: The supporting bodies yield to the

pressure exerted by the swelling bodies, thereby generating space to be used by the latter.

Here expanded mica, vermiculite, has proven to be value. It is capable of very fast transporting the acidic and alkaline media between its lamellae and then may be readily pressed together by the swelling bodies so that the resulting swelling pressures are well cushioned.

Since the swelling bodies are isolated within the mixture, they can open themselves to a substantially improved extent over that attainable once they would be accumulated. Hence, their absorptive power upon swelling is spontaneously increased.

The formulation as described by way of example displays very high absorption effects. The absorption effects were measured according to a method of the BAM [Federal Office of Testing of Materials]. Said BAM testing method is used for evaluating binders for chemicals since 1980.

For the evaluation of the absorptive capacity for various individual substances and solutions of the test material (the formulation described above) at room temperature, 1 g of each of the materials to be tested was weighed into a 250 ml Erlenmeyer flask, followed by the addition of from 20 to 30 ml of the liquid to be absorbed and by thorough mixing to accomplish uniform distribution.

After a residence time of 5 minutes, the contents of the Erlenmeyer flask was transferred onto a wire screen. The unabsorbed proportion of the liquid was allowed to drain off. After a drain-off period of 2 minutes, the amount of the unabsorbed liquid was measured.

The amount of liquid adhered to the wall of the test vessel was taken into consideration by means of a blank determination. After amount of the unabsorbed liquid had drained off, the loaded

absorbent could be taken up with the use of mechanical means (e.g. shovel).

Table

Absorptive Capacity of "Perleen 222 K10"
After 5 Minutes of Action

Substance to be absorbed	Substance Class	Absorptive Capacity: kg of Substance per 2 kg of Absorbent
Ammonia 10%	Alkaline solution	43.7
Ammonia 25%	Alkaline solution	39.0
Glacial acetic acid	Organic acid	11.8
Acetic acid 10%	Organic acid	41.5
Hydrochloric acid 10%	Inorganic acid	18.6
Hydrochloric acid 25%	Inorganic acid	20.7
Sulfuric acid 10%	Inorganic acid	20.5
Sulfuric acid 98%	Inorganic acid	38.6
Nitric acid 65%	Inorganic acid	22.9
Nitric acid 10%	Inorganic acid	18.4
Perchloric acid 70%	Inorganic acid	21.7
Perchloric acid 10%	Inorganic acid	13.5
Sodium hydroxide solution 33%	Alkaline solution	22.4
Sodium hydroxide solution 10%	Alkaline solution	17.4

A particular advantage of the absorbent according to the invention is the relative low exotherm upon the action of inorganic acids such as sulfuric acid, phosphoric acid, nitric acid and chlorosulfonic acid, so that the absorbents according to the invention are usable also with these substances. The absorbent may likewise be used for strong alkalis. No problems at all are associated with a use of the absorbent according to the invention with materials such as aldehydes, organic acids, ketones, organic

amines as well as technical fluids such as scouring agents, varnish removers, varnishes, coating compositions, diesel fuel, epichlorohydrin, fixing (hypo) baths, photographic developers and nitro thinners. Even after a period of 48 hours of storage, crumbly and lumpy products are formed which may be readily disposed of.

The period of action of 5 minutes has been pre-determined by the BAM, so that the condition of a quick applicability of binders for chemicals would be met in practice. The absorption performances detected for the examplifying formulation can even be improved by extending the period of action.

The measurements of the volume before and after the absorption demonstrate that the amount of the swelling agent still may be essentially reduced in order to avoid an increase in volume of the absorbent.

The absorbent according to the invention allows an amount of liquid to be absorbed which is up to 100% of its own volume. Thus, the dosage recommendation given to a user is easy: Employ a ratio by volume of 1 : 1 of the absorbent to the liquid to be absorbed.

The mineral supporting bodies do not only enable the liquid to be conveyed to the swelling bodies and provide these with space for opening, but they do also tack-free include said swelling bodies and protect an organic swelling agent, such as the polyacrylate used here, from the action of fire.

This formulation, by way of reducing the proportion of swelling agent therein, is also capable of efficiently protecting a hazardous good to be packaged from fire and leak-out. The nature of the mixture is such as to absorb shock. The absorbed liquid is enclosed in the swelling bodies such as to be pressure-resistant.

The formulation given by way of example has proven to be valuable in a particularly difficult test in practice. If lead sludges from battery disposal are intended to be shipped in containers for hazardous goods, sulfuric acid will once and again run off from the sludges because of the high pressure developed by the mass itself of the lead sludge.

An addition of or simple covering with the absorbent of the invention to/of the lead sludge could completely prevent the leakage of liquid sulfuric acid that would have endangered a transportation. In this case, the safety of the transportation could be substantially increased by the rapid absorptive effect, by the structure of the absorbent providing space for the swelling step and by maintaining a tack-free structure that can be strewed or shoveled.

'Overdosing' the swelling agent contained of 10%, in the place of just 2% or 3%, served to further increase chemical safety. To this end, some space for expansion had been kept free in the contaner. In practice, the absorption performance should not be completely made use of, in order to retain some external dryness of the absorbent.

If in this large scale test in practice only a vermiculite would have been used for absorption, the material would have remained wetted throughout and would not have resisted the pressure, but would have in turn released the acid. In the same manner, although using a strewable polyacrylate would have resulted in binding the acids, the amounts needed of polyacrylate would have been substantially larger and would have generated an uncontrollable swelling pressure which, upon overdosing, might have caused deformation or even disintegration of a closed container.

Moreover, the polyacrylate, once used alone by itself, would have built-up in the container to form a gel-like tacky mass, so that discharging the material and emptying the container would

have been possible only at a high and dangerous expense of cleaning.

The structure according to the invention of the absorbent has provided a particularly economical, inexpensive and safely controllable process for making transportation of hazardous goods safe.

Figure 1 shows an exploded view of the structure of the absorbent according to the invention. The supporting bodies (1) surround the swelling body (2). By the lamellar structure, the liquid is guided into the direction (3) in a capillary action towards the swelling body (2).

Figure 2, in quite a simplified presentation, shows the structure of the absorbent after swelling. The supporting bodies (1) have been pressed together by the swelling body (2) so that space has been provided for use by the swelling process.

Figure 2 to some exaggerated extent demonstrates the space-regulating effect of the vermiculite or plastic foam particles utilized as the supporting bodies (1). When these will have passed liquid to the expanding swelling bodies (2), they themselves will undergo compression. If an unrestricted volume expansion of the entire system will be allowed, for example in a container being open on the top, then the entire system will expand, the supporting bodies will be carried by the swelling bodies and will undergo no or just low deformation.

The choice of the swelling agent in such a system will depend on the liquid to be absorbed. Thus, for example, a rubber may be used as a swelling agent for binding oil by means of the process according to the invention.

The selection of the swelling agent may be illustrated by another example from practice. A variety of polyacrylates is commercially available for use in waste water technology, baby's

napkins, agrotechnology. This group of polyacrylates, designed as mere swelling agents, may be divided into two groups of applications.

The first group comprises agents anionic in character which, more specifically, will swell with water and alkali. The second group comprises agents cationic in character which will swell with acids and alkaline media, but to a minor extent in water.

This ionic behaviour and the swelling preferences may be taken advantage of in the system according to the invention.

For example, in clinical radiology and nuclear technology there are obtained waste waters which still contain radioactive elements. In most cases, the decay periods thereof are short, so that the waste waters just will have to be intermediately stored for a sufficient period of time until the radioactive radiation emerging therefrom is not dangerous any more.

Other radioactive solutions must be thickened and dumped for a long term. Irrespectively of whether such waste waters and sludges run off and will have to be immediately absorbed or are to be subjected to controlled thickening, in both cases the absorbent system according to the invention is excellently suitable.

The radioactive cationic substances contained in these waters such as, for example, ^{125}-iodine or ^{57}-cobalt, may be bound to absorbent in a particularly safe and permanent manner, once an anionic polyacrylate is used as the swelling agent, like that preferably manufactured for the baby's napkins industry.

Thereby, the radioactive materials are not only absorbed along with the waters but are also firmly bonded by the anion in the swelling system. Due to the presence of the supporting bodies, the loaded absorbent remains loose and pourable.

If, for a permanent final storage of radioactive solutions a subsequent vitrification is carried out to produce a durable enclosure, then the supporting bodies, for example, made of a fireproof vermiculite, upon a sufficient dosage, will protect the loaded swelling bodies in the vitrification procedure and will form an intimate durable bond with the glass shell.

Another example for the selection of the swelling body is constituted by drying or thickening phosphating sludges as formed in metal processing. These sludges, more specifically, contain phosphoric acid and iron. If said sludges are to be thickened under acidic conditions, then the absorbent according to the invention will be furnished with the cationic polyacrylate as a swelling agent.

If, in contrast thereto, the sludge is first neutralized with lime, so that its pH value is 6.5 or alkaline, then the anionic polyacrylate may be employed as the swelling agent in the absorbent system, whereupon a durable binding of the metals is also accomplished. As these sludges usually will be subject to final storing in a dumping site, a durable and pressure-resistent binding in the absorbent is particularly desirable. The sludges in total do not have to be treated with the absorbent; it will be sufficient that the sludge deposits are covered on the top and of the exposed lateral surfaces as desired in order to absorb any liquid that might subsequently be leaking. Thus, the transportation will besafely protected from liquid leakage.

The absorbent according to the invention and its described system is suitable for a use with any liquid and liquid-releasing sludges and pastes, acids, lyes, alkali, oils and the many hydrocarbons, ketones, esters, ethers, amines, alcohols, monomers, metal and salt solutions, emulsions, solvents, colorants and varnishes and other industrial mixtures and recovered materials and liquid-containing wastes, sludges and waste-waters.

One or more indicator dyes may be admixed with the absorbent, which indicators dissolve in accordance with the pH-value of the liquid to be absorbed, thus indicating whether, for example, an acid or base is present or the pH value is just neutral or whether an oil and/or hydrocarbon is involved. An oil-indicator dye, for example would be an oil-soluble indicator which is insoluble in water, acids and alkaline solutions. The indicator dyes may have been admixed as powders with the absorbent. An indicator dye may also be used to quickly inform a user of whether the formulation containing the suitable swelling agent would have been selected.

The absorbent according to the invention may be filled also into absorbent or barrier tubes having open pores. The entering liquid will cause the material to swell. However, the swelling pressure associated therewith will be reduced due to the internal space in the mineral providing swelling capacity. The tubes when used become impermeable for the liquid and so heavy that they are resistent to wind. In such tubes and also in packaging materials, 10% by volume of swelling agent in the mineral may be sufficient.

C L A I M S :

1. An absorbent comprising internal spaces for binding liquid harmful materials, characterized in
that the absorbent consists of supporting bodies made of an absorptive material which are not fully pressure-resistant, for example in the form of an inflated expandable mica having a lamellar structure (vermiculite), to which up to 33% by volume of one or more swelling agents have been added, said swelling agent(s) being swellable and/or soluble in the liquid to be absorbed, for example a polyacrylate and/or rubber and/or other synthetic polymer, alginate, glue, silica gel and/or bentonite, so that in the process of absorbing first the supporting bodies will cooperate in conveying the liquid to be absorbed to the admixed swelling agent and providing said swelling agent with space for swelling, and
that the absorbent is used for absorbing any liquid and liquid-releasing sludges and pastes, acids, lyes, alkali, oils and the hydrocarbons (including chlorinated and aromatic ones), ketones, esters, ethers, amines, alcohols, monomers, metal and salt solutions, emulsions, solvents, colorants and varnishes and other industrial mixtures and recovered materials and liquid-containing wastes, sludges and waste-waters and radioactive substances.

2. An absorbent comprising internal spaces for binding liquid harmful materials, characterized in
that the supporting body consists of a ground organic synthetic foam, more particularly a phenolic resin foam (PH) and/or a polyurethane foam (PUR and/or PIR) and/or a not fully pressure-resistant blend of minerals, for example vermiculite, and synthetic foam materials.

3. The absorbent comprising internal spaces for binding liquid harmful materials according to claim 1 or 2, characterized in that an acid or base may have been added to the absorbent in order to neutralize the liquid to be absorbed.

4. The absorbent comprising internal spaces for binding liquid harmful materials according to claim 1 or 2, characterized in that sodium bicarbonate has been admixed with the absorbent.

Patents Act 1977 **Examiner's report to the Comptroller under Section 17** **(The Search report)**	Application number GB 9519044.3
Relevant Technical Fields (i) UK Cl (Ed.N) C3V (VCX, VDS, VDX) (ii) Int Cl (Ed.6) B01J **Databases** (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE: WPI	Search Examiner K MACDONALD Date of completion of Search 6 DECEMBER 1995 Documents considered relevant following a search in respect of Claims :- 1

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 1597035	(MITSUBISHI) Claims 1 to 7	at least Claim 1
X	US 5030591	(COLE) Claim 1; column 3, lines 24 to 35	at least Claim 1
X	US 4914066	(HOECHST CELANESE) Claim 1	at least Claim 1
X	WPI Abstract Accession Number 80-22860C/13 & JP 55022312 A (MITSUBISHI) 18.02.80 (see Abstract)		at least Claim 1

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